

JAN 12 2010

Nalco Docket No. 7774
Customer No. 49459In the United States Patent and Trademark Office

Applicants:	Brian T. Holland et al.)	Examiner:	Daniel S. Metzmaier
)		
Serial No.:	10/827,214)	Art Unit:	1796
)		
Date Filed:	April 19, 2004)		

For: COLLOIDAL COMPOSITIONS AND METHODS OF PREPARING SAME

Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

**DECLARATION OF PRIOR INVENTION IN THE UNITED STATES OR IN A NAFTA OR
WTO MEMBER COUNTRY TO OVERCOME CITED PATENT OR PUBLICATION
UNDER 37 C.F.R. § 1.131**

Dear Sir:

This Declaration is to establish completion of the invention in this application in the United States prior to December 5, 2003, the effective date of Cundy et al., "Some observations on the preparation and properties of colloidal silicates. Part I: synthesis of colloidal silicalite-1 and titanosilicalite-1 (TS-1)," Microporous and Mesoporous Materials, 66 (2003): 143 to 156 ("Effective Date of Cundy").

To establish a date of completion of this invention prior to the Effective Date of Cundy, Applicants submit herewith copies of research notebook pages attached as Exhibit A hereto. This exhibit clearly and definitely establishes invention of the subject matter of the currently rejected claims prior to the Effective Date of Cundy.

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Applicants declare that the document submitted herewith as Exhibit A is dated prior to December 5, 2003. Accordingly, Applicants respectfully assert that this invention was completed prior to the Effective Date of Cundy.

Explanations of the experiments portrayed on pages 1 to 3 of Exhibit A is provided below:

Notebook Page 3 [Page 1 of Exhibit A]

Preparation of Ce₂O₃-SiO₂ co-sol

Ce(III) stock solution:



$$\frac{\text{Ce}_2\text{O}_3}{2 \text{ Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O}} = \frac{328.24}{868.46} = 0.3779$$

For 5%Ce₂O₃ solution:

$$5/0.3779 = 13.23 \text{ g of cerium nitrate in 100g}$$

Synthesis: Acid sol or silicic acid was prepared by deionizing sodium silicate. The yield was 1.1 kg of acid sol with a specific gravity of 1.042. Silica concentration was calculated using the equation:

$$\% \text{SiO}_2 = \text{Specific gravity} * 163.2207 - 163.1891$$

$$\text{Total silica} = 1.1 * 6.88\% = 75.75 \text{ g}$$

0.75 g CeO₂ is 1%, thus 15g of Ce stock solution was needed.

The acid sol had a 3.05 pH and a 195μS conductance, with the addition of the acidic Ce solution these changed to 2.95 and 980 respectively. This blend was a true solution of ionic Ce(III) and monomeric silicic in an aqueous medium. The complete incorporation of both species in solution is the basis for the homogeneous formation of the corresponding colloidal oxides under the high pH reaction conditions.

- Heel – 200 ml of deionized water and 0.7 g of 45% KOH solution; pH 13.34. Heated to 75°C with steering.

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- Feed – The acid sol/Ce was fed to the heel at 3.66 ml/min once the temperature in the heel reaches 76°C. The pH is monitor; after 1:15 the pH has dropped from the original 11.3 to 7.9. At this time a solution of 0.1N KOH was co-fed to maintain the pH above 7.3. After 4:57 hours both solutions have been added, final pH is 7.3 at 75°C. Heating with stirring continued for 2 hours.
- Concentration – The 2 liter pinkish sol was concentrated to 300 ml by ultra filtration. The filtrate was colorless, indicating that all the Ce was in the colloidal particles

Notebook Pages 17 and 18 [Pages 2 and 3 of Exhibit A]

Preparation of $\text{TiO}_2\text{-SiO}_2$ co-sol

Synthesis: 1100 g of acid sol was prepared from sodium silicate. Specific gravity was 1.04, corresponding to 6.56% SiO_2 .

Total silica = $1.1\text{kg} * 6.56\% = 72.42\text{g}$

2% $\text{TiO}_2 = 1.44\text{ g TiO}_2$

TiO_2 solutions prepared from TiOSO_4 formed a precipitate with time; so it was not practical to store the solutions.

A solution of 3.3g of 87% $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ was dissolved in 150 ml of deionized water and was added to the acid sol. This homogeneous metal and silicic acid solution was used as feed for the colloidal particle synthesis.

- Heel – 200 ml of deionized water and 0.7 g of 45% KOH, 12.47 pH at room temperature. Heated with steering to 77°C.
- Feed – The silica-Ti solution is added to the heel at 3.66 ml/min. After 30 minutes a co-feed of 0.1N KOH started. At the end of the reaction, 4 1/2 hours, a total of 500 ml KOH were added. The sol was refluxed for one hour
- The dilute sol was milky white and was concentrated by ultra filtration. The excess ions were washed out by dial filtration. Three 1-liter filtrates are collected. Analyses confirmed that the TiO_2 was incorporated into the colloidal particle.

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Ion	SiO ₂	Na	K	SO ₄	Ti
ppm					
1 st filtrate	350	6.4	440	920	7.9
2 nd filtrate	200	4.6	300	630	3.2
3 rd filtrate	87	2.4	150	340	0.9
Sol			880	190	1,200

The resultant sol was stable for over two years.

DECLARATION

As a person signing below, I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated: 1/11/10

Signed: 
Yolanda Ortiz

Exhibit A

Page 1 of 3

TITLE $\text{Ce}_2\text{O}_3/\text{SiO}_2$

PROJECT NO.

BOOK NO.

3

Preparation of $\text{Ce}_2\text{O}_3\text{-SiO}_2$ Co-sol

$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ \rightarrow Ce_2O_3 Ce_2O_3 $328.24 = 375.9$
 424.23 328.24 $2 \text{ Ce}(\text{NO}_3)_3$ 867.46

5% Ce_2O_3 soln; $5/375.9 = 13.23 \text{ g}$ of substrate
 $\text{pH} = 7.12$

NO_3 186 3 mg NO_3 0.0069 mg/g
 $\text{Ce}(\text{NO}_3)_3$ 424.23 439.235 0.091 mg/g 1% soln
 $= 0.428 \times 13.23 \text{ g} = 5.66 \text{ g}$ NO_3 9.1 mg/g 100 g of 5% Ce_2O_3
 0.9 mg/g

$7 \text{ g KOH} + 200 \text{ ml DIW}$ $\text{pH} 13.34$ $T = 19.5$

$\text{AS } 1.12$ 11 kg $\text{pH} = 9.05$ $C = 195$ $T = 98.0$

$\text{SA } 2.042$ 6.88 g $\text{O}_2 \times 11 \text{ kg}$ $75.75 \text{ g} \times 1\% = 7.57 \text{ g}$ Ce_2O_3 11.15 g Ce_2O_3 soln

T	W	E	N	A	pH	T
9:30	33.7	9.92	7.6	3.66 ml/min	9/mg per g $\times 1.5 \text{ g} = 13.7 \text{ mg}$	NO_3
2:01	95	9.26	7.4	turn	addition	
1:02	22.3	8.23	7.3	125 ml	DIW KOH in place	
1:15	20.0	7.9			addition KOH starts	
1:29	32.2	8.21	7.3	50 ml	on 5 mg	
1:53	4.1	7.79	7.5	75		
2:09	4.67	7.85	9	90	1.75 g Ce_2O_3	$140.12 \text{ g} = 8.83$
2:27	53.5	7.99		125		528.24
3:10	68.9	7.35		5	$= 6.40 \text{ mg Ce}$	
3:24	73.8	7.40		40		
3:45	81.6	7.44		75		
4:02	87.5	7.60		93		
4:18	90.6	7.30		105		
4:57	107.5	7.90		125		

heated an ultra flow

$2/6$ $\text{pH} = 7.30$ $T = 19.5$ Ce_2O_3 ppt on and desirable

$\text{pH} = 7.40$ $C = 940$ pH pH pH

$\text{N } 100 \text{ ml}$ pH pH pH pH

$2/7$ 1 g pH 1.25 pH 1.25 pH 1.25 pH 1.25

pH 4.40 pH 8.54 pH 8.54 pH 8.54 pH 8.54

3 ml pH 7.27 pH 7.27 pH 7.27 pH 7.27

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Exhibit A
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TITLE $\text{SiO}_2/\text{TiO}_2$
Co - Sol

PROJECT NO.
BOOK NO.

17

Residue with TiO_2SO_4

AS = 1100g $C = 215$ miles $\text{pH} = 2.32$
 Sp. Gr. 1.04 6.56% SiO_2
 1100g 6.56% = 72.48g SiO_2 $\times 2\% \text{TiO}_2 = 1.44\text{g}$ 1.10g
 $\Rightarrow 3.3\text{g}$ $\text{TiO}_2\text{SO}_4 \times \text{H}_2\text{O}$ from GFS 150g 3rd
 after 40 AS $\Rightarrow \text{pH} = 1.70$ $C = 950$ $T_1 = 863\text{mg}$

Next
 0.75 KOH $\text{pH} = 1.70$ 11.05
 500 ml SiO_2 12.47g H_2O 70°C

t	val	pH	T	
0	0	12.05	77	3.66 ml/min
10	37	9.55	72	
50	22	8.90	72	
32	118	7.96	73	addition of 0.1N KOH starts
41	151	7.20		20 ml added
1:06	241	6.34		40
1:13	267	5.84	73	50
1:25	312	6.2		100 Feasibility Model app
1:50	402	6.8		185
2:13	485	7.12	74	250
2:25	531	6.79		250 ml made in the front
2:40	589	6.42	74	15
3:03	671	6.80		100
4:00	878	6.67	72	225
4:37	1021	6.17	74	250 stop
5:45		6.24		Replaced for 1-hr
3:15		7.10	77	

Very Feasible, no ppt on gel
 $\text{pH} = 6.5$ $C = 1310$
 V.F. plants

3/28 Filter very slow
 1st filtrate 350 ml $\text{pH} = 5.60$ $C = 1350$
 500 ml added to the cell
 2nd filtrate 930 ml $\text{pH} = 5.76$ $C = 950$
 4/15
 3rd filtrate
 710 ml $\text{pH} = 6.15$ $C = 520$

Continued pg 18

SIGNATURE

DATE

READ AND UNDERSTOOD BY

DATE

cep

Cheryl Slobogoshi

Exhibit A
Page 3 of 3

18

TITLE

PROJECT NO.
BOOK NO.

Concentrate

Very thick, but fluid opaque

300 ml 3 of 90-6.55

set in test tube @ 40°C as 18A

A

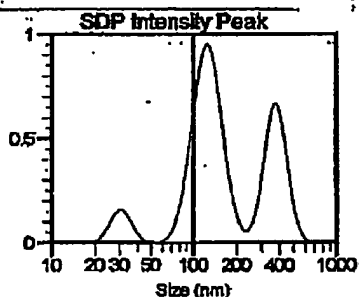
pH = 6.53

After overnight @ 60°C, samples look like gel but re-disperse when shaken. pH released @ 10.3 w/ NH₃

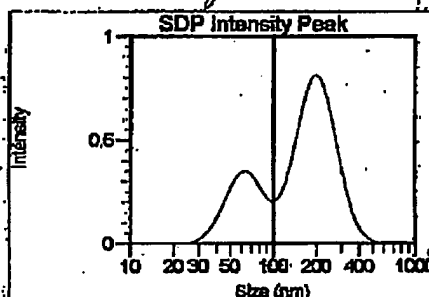
DLS data:

114.2 ± 49 nm
poly 0.701

133.3 ± 56.8 nm
poly 0.701



Amount	Size (nm)	SD (nm)
60.8%	121.3	22.6
31.9%	363.3	49.9
7.3%	29.4	3.9



Amount	Size (nm)	SD (nm)
70.7%	186.4	50.8
29.3%	61.8	15.4

A Concentrate

B Dilute pH adjusted

Analyses Report

	SiO ₂	Na	K	SO ₄
1st fill	350	6.4	490	92.57
2nd	200	4.6	300	430
3rd	87	2.4	150	340
4th			800	190
5th			460	18

RT samples both thick, re-disperse w/ shaking

17.9 13.2 0.9 1200 900

± Potential @ 7.9 - 3961

Stable after 2 years

SIGNATURE

DATE

READ AND UNDERSTOOD BY

DATE

UPP

Chen Shubao